

Recommended SJR OP Pesticide TMDL Compliance Monitoring¹

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October 4, 2005

In mid-September, the Central Valley Regional Water Quality Control Board (CVRWQCB) held a workshop concerning a proposed Basin Plan amendment for regulating diazinon and chlorpyrifos in the mainstem San Joaquin River (SJR). An issue of concern noted at that workshop was the lack of specificity for the compliance monitoring program that the Regional Board staff will propose associated with implementation of the diazinon and chlorpyrifos TMDLs. The CVRWQCB staff proposed deferring providing information on compliance monitoring until after adoption of the Basin Plan amendment. This delay is inappropriate because the method of assessing TMDL target compliance is a critical component of the TMDL. Detailed information on how compliance will be assessed should not be separated from the adoption of the TMDL into the Basin Plan. Without such information, it will not be possible to evaluate the adequacy of the proposed approach for controlling the aquatic life toxicity caused by the OP pesticides, diazinon, or chlorpyrifos, or the replacement of these chemicals by other pesticides that could cause aquatic life toxicity in the SJR.

Need for Information on the Proposed TMDL Compliance Monitoring

The Regional Board should specify the initially proposed characteristics of the SJR OP Pesticide TMDL compliance monitoring program. This would include the anticipated compliance points for the monitoring program, parameters to be measured, analytical methods and their sensitivity for reliably detecting the regulated chemicals, frequency of measurements, etc. With such information it will be possible to evaluate whether the proposed compliance monitoring could be expected to be adequate for detecting significant violations of the requirements set forth in the TMDL.

Dormant Pesticide Applications

One of the issues of concern regarding compliance monitoring is the application of dormant-spray pesticides to orchards just prior to major stormwater runoff events. In order to adequately monitor for potential discharges from dormant spray applications there is need to develop a technically valid approach for determining worst-case violations of the use of these pesticides. Agricultural interests will likely be able to control stormwater runoff of these pesticides during low to moderate runoff events. However, as Lee (2005) indicated in his comments on the draft DPR proposed regulations governing dormant application of the OP pesticides, there will be runoff events associated with large storms, when violations of the TMDL goal will likely occur following application. It is under such conditions that there is the greatest potential for high concentrations of OP and other pesticides to be present in runoff from fields, even when the DPR proposed required application restrictions are followed. In order to

¹ Reference as Lee, G. F., and Jones-Lee, A., "Recommended SJR OP Pesticide TMDL Compliance Monitoring," Submitted to William Jennings California Sportfishing Protection Alliance, Report of G. Fred Lee and Associates El Macero, CA October (2005).

provide a technically valid assessment of compliance with the TMDL target goals, the compliance monitoring should specifically include monitoring immediately after major runoff events when there is the greatest likelihood of failure to comply with TMDL targets.

Non-Dormant Applications

The runoff/discharges following application of chlorpyrifos and/or other pesticides in the spring, summer and fall should be monitored to determine whether violations of chlorpyrifos the water quality objective occur. As part of developing the application protocol for non-dormant pesticides an examination should be made of the conditions that have in the past led to aquatic life toxicity or violations of the TMDL target goals for non-dormant pesticide. The compliance monitoring regimen should include periodic examination of how pesticides are being used in the San Joaquin River watershed. This information should be used to guide development and implementation of the ongoing TMDL compliance monitoring program.

Monitoring Methodology

The TMDL compliance monitoring should include determination of the total amount of aquatic life toxicity measured in a sample and how much of that toxicity can be accounted for based on the concentrations of diazinon and chlorpyrifos found in the sample. This type of monitoring was used in the studies we conducted in the mid-to-late-1990's in the Upper Newport Bay—Orange County California stormwater runoff monitoring for the Santa Ana Regional Water Quality Control Board. Reports on those studies are available at <http://www.gfredlee.com/punbay2.htm>. These interactive studies involved working closely with the laboratory doing the toxicity testing to determine the total toxicity in the sample; when a sample showed enough toxicity to kill several of the test organisms in one to two days, the study plan called for follow up testing on that sample.

TMDL compliance monitoring should similarly incorporate a requirement that for each sample that shows potentially significant short-term toxicity, a fairly complete GC analysis of the sample be conducted to determine the amounts of the OP pesticide and carbamate pesticides present in the sample. With that information and by conducting additional toxicity testing on a refrigerated stored sample of the water of concern in a dilution series with and without piperonyl butoxide (PBO) at 100 µg/L, it is possible to determine how much of the toxicity may be caused by the OP pesticides (diazinon and chlorpyrifos). The inclusion of PBO in some of the test samples is part of a directed toxicity identification evaluation (TIE) procedure designed to determine whether the toxicity found is likely due to an OP pesticide.

If there are elevated concentrations of potentially toxic heavy metals relative to US EPA water quality criteria, their toxicity can be evaluated through the addition of EDTA to the sample. If some/all of the toxicity disappears upon the addition of EDTA, it is likely that one or more of the heavy metals is the cause of at least some of the toxicity found in the sample. This approach was used by Lee and Taylor (2001a) to find that the heavy metals

in the urban and rural stormwater runoff was not the cause of the aquatic life toxicity found in this runoff.

It is important to measure diazinon and chlorpyrifos concentration with adequate sensitivity to detect their presence at potentially toxic levels considering the additive toxicity of diazinon and chlorpyrifos and other OP and carbamate pesticides. The US EPA 8141 Special Low-Level gas chromatographic procedures with an increased evaporation step in order to achieve higher sensitivity can be used for this purpose. The University of California, Davis Aquatic Toxicology Laboratory has been using ELISA procedures which have a lower detection limit for diazinon of about 30 ng/L and for chlorpyrifos of about 50 ng/L.

Through a sample dilution series (e.g., 100%, 50%, 33%, 25%, 20%, 16.6%, 12.5% and, for highly toxic samples, 6.25%) of the sample should be tested in the presence and absence of PBO in the sample, it should be possible to detect whether pyrethroid pesticides present in the sample are contributing to the aquatic life toxicity in the sample. Use of this approach in our Orange County Upper Newport Bay studies revealed that there was a substantial amount of toxicity caused by unmeasured/unidentified chemicals or conditions that needed to be addressed through further TIE studies (Lee and Taylor (2001b).

The US EPA methods (US EPA, 2002a,b,c) should be used for the toxicity testing done using *Ceriodaphnia* and for some samples, fathead minnow larva. For samples that could involve discharges to marine/estuarine waters, the toxicity testing should be conducted with mysids after adjusting the salinity of the freshwater to 20 parts per thousand using sodium chloride.

Sediment Toxicity

The OP pesticide TMDL compliance monitoring should include sediment toxicity testing using the US EPA (2002d) procedure using *Hylella azeteca* as the test organism. Only the acute testing procedure should be conducted since the chronic testing procedure has been found by Weston (2005) to be unreliable.

Aquatic Life Toxicity Monitoring for Non-TMDL Pesticide Situations

The recommended TMDL compliance monitoring program presented herein is also applicable to all aquatic life toxicity monitoring in stormwater runoff, and fugitive water and tail water discharges. Monitoring programs that only measure water column toxicity without the follow up monitoring recommended herein fails to provide the information needed to provide magnitude of the toxicity and its potential cause.

References

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